10/511828
DT05 Rec'd PCT/PTO 20 OCT 2004

EASY-CLEAN COOKING SURFACE AND ELECTRICAL HOUSEHOLD APPLIANCE COMPRISING SUCH A SURFACE

The present invention relates to the field of articles intended for the preparation and cooking of food and more particularly the cooking surface of these articles that is in contact with the food to be processed.

For many years, significant efforts have been developed in order to facilitate the everyday preparation of meals. Among the notable progress, coatings, or claddings, based on fluorocarbonated polymers as non-stick coating in kitchen utensils quickly developed since the end of 1950. Such coatings are universally known since the process presented in the patent FR 1120749 allowed a sure fixing of such coatings on various metals, such as aluminum.

However, such coatings remain fragile. Thus, easy ways were developed in order to mechanically reinforce the layer on its support. Many improvement patents describe methods and means making it possible to increase the scratch resistance of such coatings, by acting on the coating and/or on the substrate. Even so, such coatings remain sensitive to the repeated use of sharp or pointed metallic materials, such knives or forks.

At the same time, developments were carried out on mechanically resistant surfaces for which it was attempted to improve the ease of cleaning. Metal deposition, such as chromium plating on stainless steel, quasi-crystals, or nonmetallics (silicates,...) thus appeared.

Quasi-crystals are a phase or metal compound presenting, at the crystallographic level, symmetries of rotation of the axis of the order 5,8, 10 or 12, as icosahedral and decagonal phases. Such coatings are in particular described in patent EP 0 356 287 and have qualities of scratch resistance, even non-stick in certain cases.

In addition, the document FR 2784280 describe a composite cooking surface constituted by two phases, ceramic and metal, intended to bring to treated kitchen utensil bottoms a non-deformability in their range of use, as well as a good wear resistance. However, such coatings do not have very good performance with regard to ease of cleaning, so that the addition of a solid lubricant, such PTFE, is often recommended when this function is required. This additional step involves overall a significant cost for the development of such a cooking surface.

The present invention aims at overcoming the above mentioned disadvantages of the prior art, by proposing a cooking surface with scratch resistance, ease of cleaning, corrosion resistance characteristics.

The present invention is achieved by a food cooking surface for a kitchen utensil or cooking appliance, characterized in that this cooking surface is of an amorphous metal alloy.

The use of amorphous metal alloys, also called metal glasses brings interesting properties in term of surface properties (hardness in particular), and corrosion resistance. Indeed, the absence of a crystalline phase leads to the absence of crystalline solid defects (dislocations, grain boundary...) and the phenomena induced by these defects (in particular corrosion at the grain boundaries).

According to the formulation and the manner of producing the alloy, the presence of a nanocrystalline phase can observed. However, the nanocrystalline structure has properties close to the amorphous structure, by the absence of atomic order at large distance, at least with regard to the desired characteristics, such as previously mentioned. One could even expect a slight improvement of the hot behavior, in particular with regard to its hardness.

In a surprising way, it was noted, during tests, that some amorphous metal alloy coatings also presented properties of ease of cleaning, which can also be expressed by the possibility of easily removing elements carbonized on the cooking surface. However, among these alloys, some are not compatible with food contact.

Thus, advantageously, the alloy has the formula $A_aD_bE_cX_d$ in which:

- A is one of the elements Zr or Cu,
- D is at least one element chosen from the group consisting of Ni, Cu, Al if A is Zr or at least one element chosen from the group consisting if Ni, Zr, Al if A is Cu,
- E is at least one element chosen from the group consisting of Ti, Hf,
- X represents the impurities of production, with:
    - $40\ \% < a < 70\ \%$ at,
    - $5\ \% < b < 30\ \%$ at,
    - $c < 10\%$ at,

- $d < 1$ % At, and

$a+b+c+d = 100$ % at.

It is significant to note that this selection has already been carried out among alloys being able to made amorphous. Moreover, other elements have voluntarily been put aside by their toxicity with respect to humans. The coatings proposed thus do not supply any toxicity to food in contact, even brought to high temperature.

In addition, the selection of the components of alloy also took account of the elements which support the germination of crystals, in order to limit this phenomenon.

The contents of various elements are the result of the fabrication conditions, supplemented by tests concerning the abrasion resistance and the ease of cleaning of such coatings after difficult cooking.

Account is also taken of eutectic compositions that have a low melting point as well as a lower viscosity of the liquid, favorable to obtaining the amorphous state.

Various tests have shown in an unexpected way that a significant proportion of zirconium makes it possible to obtain coatings presenting an exceptional ease of cleaning.

Moreover, studies have shown that the alloys comprising at least three elements are more stable than binary alloys, and are all the more stable as the number of elements is large.

The alloys obtained remain in particular stable, without structural transformation, when they are brought up to temperatures of the order of 300° C, temperatures that are higher than the temperatures usually used for food cooking.

In addition, zirconium also makes it possible to further increase the thermal stability of the final alloy.

According to an advantageous realization of this invention, the metal alloy is of the formula $Zr_aCu_bNi_cAl_dTi_eX_f$, where a, b, c, d, e, are the respective proportions of Zr, Cu, Ni, Al and Ti in the alloy, said proportions being comprised within the following ranges:

- $40\ \% < a < 70\ \%$
- $10\% < b < 25\%$
- $5\% < c < 15\%$
- $5\% < d < 15\%$
- $2\% < e < 10\ \%$,

and where x represents the impurities of production, with $f < 1\ \%$ at.

In this formulation, $a+b+c+d+e+f = 100\ \%$ at.

The elements entering into the composition of these alloys were selected in particular so that the corresponding alloy has a high vitreous transition temperature. The compositions were a priori defined to approach the compositions corresponding to eutectics in order to decrease the temperature of the liquid, which allows lower speeds of cooling to obtain the amorphous state with or without the presence of nanocrystalline phase.

Of course, the composition of alloys was also adjusted according to the intended properties of mechanical strength,

corrosion resistance and ease of cleaning of the alloy obtained.

According to a first mode of implementation of the invention, the food cooking surface of the kitchen utensil or cooking appliance is obtained by the deposit of a suitable thickness of metallic material on a substrate. This deposit can be carried out by one or the other of the following processes: thermal projection of a powder of adequate granulometry, deposit by electrophoresis of a micro or submicronic powder, cathode sputtering of a massive target. In this last case the target can be obtained by assembly on a copper substrate of one or several sheets or plates of a material having the desired composition, said sheets or plates being obtained either by powder sintering or thermal projection of powder, or resulting from casting. Other techniques, such as hot compaction or the deposit by electrolyses also can be used.

This implementation has the advantage of using little material and of being able to adjust the thickness of the cooking surface.

All of these techniques make it possible, in addition, to obtain deposits having strong cohesion with the substrate on which they are deposited. The risks of degradation of the deposit by pointed objects of the knife or fork type are thus very low.

The material deposited in the processes previously described can result from a powder, amorphous from the start or obtained by grinding of a crystallized alloy, said powder then undergoing a step of vitrification before the depositing step or at the time of the depositing step, according to the

technique used. In this procedure, the idea is thus to obtain the amorphous phase at the very end.

According to a second mode of implementation of the invention, the food cooking surface of the kitchen utensil or cooking appliance is obtained by assembly of an amorphous alloy sheet with or without the presence of a nanocrystalline phase on a substrate. This implementation has the advantage of approaching the known implementations for assembly of metals, which makes it possible to be able to adapt known techniques without significant specific development.

According to a procedure, the sheet is obtained by rolling of an amorphous ingot resulting from melting of a mixture of metals. It is particularly favorable, from an economic point of view, to use the method of melting then rolling, in particular in the case of amorphous materials, because they show a significant rate of reduction by rolling, with controlled temperature.

According to another process of development, the sheet is obtained by the technique of solidification on a wheel.

This technique, by solidifying metal alloy on a cooled wheel driven in rotation, makes it possible to obtain sufficiently high cooling speeds so that an amorphous film can formed. The thicknesses obtained, being able to reach 0.1 mm, are completely compatible with the use envisioned, without it being necessary to carry out a later rolling.

In this second mode of implementation of the invention, the assembly of the sheet on the substrate is carried out by one of the following techniques: colaminating, brazing, hot striking, in a manner known *per se*.

Advantageously, the sheet and the substrate undergo, after assembly, a step of forming by stamping.

Other advantages resulting from the tests will appear from a reading of the description that will follow, in relation to an illustrative example of the present invention given as a non-limiting example.

The example of realization of the invention relates to a massive amorphous alloy substrate of composition$Zr_{60}Cu_{17.5}Ni_{10}Al_{7.5}Ti_5$ obtained by melting in an inductive crucible of a massive ingot cooled in a copper mould according to conditions leading to the formation of an amorphous alloy. One face of this substrate underwent an intensive polishing, approximating an optical polishing, before the performance of tests, in order to make it comparable with other cooking surfaces so that the tests for evaluation of the ease of cleaning such a surface, in a domestic cooking use, can be compared.

The system for evaluation of the ease of cleaning makes it possible to quantify the capability of a cooking surface to be restored to its original appearance after use. This system for evaluation comprises the following steps:

- surface is locally covered with a food mixture of known composition,
- this mixture is carbonized, or burnt, in a furnace under defined conditions, for example 210°C for 20 minutes,
- after cooling, the surface is caused to soak during a controlled time in a mixture of water and detergent,
- an abrasive pad is then applied under a defined constraint using an abrading apparatus (plynometer) to the soiled surface in a back and forth movement for a given number of cycles,

- the percentage of correctly cleaned surface is noted and characterizes the ease of cleaning of the cooking surface.

The tests carried out on various types of surface thus make it possible to comparatively evaluate the quality of the surfaces as regards their ease of cleaning.

Of course, the tests are carried out by respecting the same parameters for each step of the system of evaluation: same food mixture, same surface to which the food mixture is applied, same temperature of carbonization,...

The following comparative table shows the results obtained on three different cooking surfaces, namely polished stainless steel, quasi-crystals, and the amorphous alloy of formulation $Zr_{60}Cu_{17.5}Ni_{10}Al_{7.5}Ti_5$ such as previously described, in a severe test with a food composition based on milk and rice considered to be difficult to clean once carbonized. Such a test thus makes it possible to highlight well the differences between cleaning quality of the surfaces.

	Polished stainless steel	Quasi-crystals	Amorphous
Quantity of carbonized residue removed	25%	30%	90%

The table shows without ambiguity the exceptional results obtained with the amorphous alloy.

It should be noted that the number of cycles of abrasion on the plynometer was fixed at 10. This low number of cycles

highlights well the quality of ease of cleaning of the amorphous surface since there remains no more than 10 % of the soiled surface after only 10 back and forth passes of the abrasive pad.

Repetitive tests after complete cleaning of the surface show that the ease of cleaning of the amorphous alloy is not altered.

When the implementation of the invention implies the use of a substrate, this one is then composed of one or more metal sheet(s) of the following materials: aluminum, stainless steel, cast iron, steel, copper. However, the present invention is not limited to the realization of a layer of small thickness of an amorphous metal alloy with or without the presence of a nanocrystalline phase deposited or assembled on a thick substrate, but also aims at the realization of massive material, with or without a substrate, this latter, when it is present, not having a mechanical supporting role for the layer, but assuring another function, such as the thermal distribution of heat for a utensil placed on a heat source (frying pan, sauce pan,...).